

THE GROUND STATE ENERGY OF HEAVY ATOMS: RELATIVISTIC LOWERING OF THE LEADING ENERGY CORRECTION

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ABSTRACT. We describe atoms by a pseudo-relativistic model that has its origin in the work of Chandrasekhar. We prove that the leading energy correction for heavy atoms, the Scott correction, exists. It turns out to be lower than in the non-relativistic description of atoms. Our proof is valid up to and including the critical coupling constant. It is based on a renormalization of the energy whose zero level we adjust to be the ground-state energy of the corresponding non-relativistic problem. This allows us to roll the proof back – by relatively simple technical means – to results for the Schrödinger operator.

1. INTRODUCTION

The energy of heavy atoms has attracted considerable interest that dates back to the advent of quantum mechanics. As in classical mechanics it soon became clear, that the exact solution of problems involving more than two particles interacting through Coulomb forces is not possible. Thomas [60] and Fermi [22, 23] introduced their description of such atom by the particle density and Lenz [31], who wrote down the corresponding energy functional which we will use here (see (7)), addressed this question and derived that the ground state energy of atoms should decrease with the atomic number Z as $Z^{7/3}$. Scott predicted that this could be refined by an additive Z^2 -correction. Considerably later Schwinger [46] argued also for Scott's prediction. Schwinger [47] and Englert and Schwinger [10, 11, 12] even refined these considerations by adding more lower order terms (see also Englert [9]).

The challenge to address the underlying question whether the predicted formulae would yield asymptotically correct results when compared with the N -particle Schrödinger theory was for a long time unsuccessful. It were Lieb and Simon who proved in their seminal paper [36] that the prediction of Thomas, Fermi, and Lenz is indeed asymptotically correct. Alternative proofs were given by Thirring [59] (lower bound), Lieb [33], and Balodis and Solovej [40]. The Scott correction was established by Hughes [26, 27] (lower bound), and Siedentop and Weikard [48, 49, 50, 51, 52] (lower and upper bound). In fact, even the existence

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of the $Z^{5/3}$ -correction conjectured by Schwinger was proven (Fefferman and Seco [18, 19, 20, 13, 21, 16, 14, 15, 17]). Later these results were extended in various ways, e.g., the Scott correction to ions (Bach [1, 2]), to molecules (Ivrii and Sigal [29], Solovej and Spitzer [58, 57], Balodis [4]), and to molecules in the presence of magnetic fields (Sobolev [55] and Ivrii [30]). Ivrii [28] extended the validity of Schwinger's correction to the molecular case.

Nevertheless, from a physical point of view, these considerations are questionable, since large atoms force the bulk of the electrons on orbits that are close to the nucleus (of order $Z^{-1/3}$) where the electrons move with high speed which requires a relativistic treatment. Schwinger [47] has estimated this effect concluding that they should contribute to the Scott correction whereas the leading term should be unaffected by the change of model. Sørensen [44] was the first who proved that the Thomas-Fermi term is indeed left unaffected when the non-relativistic Hamiltonian is replaced by the Chandrasekhar operator in the limit of large Z and large velocity of light c . Cassanas and Siedentop [5] showed, that similarly to the Chandrasekhar case, the leading energy is not affected for the Brown-Ravenhall operator.

Recently, Solovej, Sørensen, and Spitzer [56] announced a proof that a correction is at most of the order Z^2 although no claim on the actual value of the coefficient was made. (See also Sørensen [43] for the non-interacting case). In the present paper, we give an alternate proof of the Scott correction of the Chandrasekhar operator, which we present – for simplicity – in the atomic case. Our proof relies heavily on semi-classical approximation for electrons that are far enough from the nucleus. However, we use them only indirectly relying on known results about the non-relativistic Scott correction. In addition we use only relatively standard technical means as Lieb-Thirring and Hardy inequalities. Our basic strategy is a renormalization of the energy setting the energy of the Schrödinger atom as zero. Moreover, we are able to extend the result of [56] to the case of the critical coupling constant. In view of the corresponding situation for the Dirac operator (see Remark (3) after Theorem 1.1), this is a subtle and not at all obvious observation.

However, the question of whether the Schwinger correction which lives on the scale $Z^{-2/3}$ also exists in this relativistic model and – if so – cannot be answered with our techniques and is, therefore, left open.

The energy of an heavy atom is described by a quadratic form

$$(1) \quad \mathcal{E}^\# : \mathfrak{Q}_N \rightarrow \mathbb{R}$$

$$\psi \mapsto \left\langle \psi, \left[\sum_{\nu=1}^N (T^\# - Z|x|^{-1})_\nu + \sum_{1 \leq \mu < \nu \leq N} |x_\mu - x_\nu|^{-1} \right] \psi \right\rangle$$

with

$$(2) \quad \mathfrak{Q}_N := \bigwedge_{\nu=1}^N C_0^\infty(\mathbb{R}^3) \otimes \mathbb{C}^q.$$

The superscript $\#$ refers to the following two operators which are self-adjointly realized in $L^2(\mathbb{R}^3) \otimes \mathbb{C}^q$:

$$\begin{aligned} \text{Chandrasekhar operator: } T^C &:= \sqrt{c^2 p^2 + c^4} - c^2 \\ \text{Schrödinger operator: } T^S &:= \tfrac{1}{2} p^2. \end{aligned}$$

The parameter $q \in \mathbb{N}$ represents the possible number of spin states per electron which – physically – has the value 2; Z is the atomic number, c is the velocity of light, N is the electron number. We use units in which $m = e^2 = \hbar = 1$.

A word about names: we address operators of the form $T^C + V$ with a potential V as Chandrasekhar operators, since the use of this kinetic energy can be traced back at least to Chandrasekhar's semiclassical treatment of the stability of stars [6] where it can be viewed as the underlying operator. Later the use of T^C has been investigated by Weder [61] and by Herbst [25]. In the literature the operator is sometimes addressed as pseudo-relativistic operator or Herbst operator.

In the following we assume that the system is neutral, i.e., $Z = N$, an assumption that we make mainly because of notational convenience. It follows from Kato's inequality (with sharp constant), $(2/\pi)|x|^{-1} \leq |p|$, that the Chandrasekhar form \mathcal{E}^C is bounded from below, if and only if

$$(3) \quad \kappa := Z/c \leq 2/\pi.$$

Henceforth we assume this condition.

The ground state energy of a heavy atom with atomic number Z is given by

$$(4) \quad E_{(\kappa)}^\#(Z) := \inf\{\mathcal{E}^\#(\psi) \mid \psi \in \mathfrak{Q}_N, \|\psi\| = 1\}$$

where $\#$ refers – as above – either to the Chandrasekhar or the Schrödinger operator, the former being dependent additionally on κ . We are interested in $E_\kappa^C(Z)$. However, $E^S(Z)$ will also play an essential role, namely in regularizing the energy. Note that $\mathcal{E}^C \leq \mathcal{E}^S$, which implies that $E_\kappa^C(Z) \leq E^S(Z)$. Our main result strengthens a result by Solovej, Sørensen, and Spitzer [56] in the atomic case to the critical value of the coupling constant.

Theorem 1.1. *Let $\kappa \in (0, 2/\pi]$ and $q \in \mathbb{N}$. In the limit $Z \rightarrow \infty$ with $\kappa = Z/c$ fixed and $N = Z$,*

$$(5) \quad E_\kappa^C(Z) = E^S(Z) - qs(\kappa)Z^2 + o(Z^2)$$

where

$$(6) \quad s(\kappa) := \kappa^{-2} \operatorname{tr} \left[\left(\sqrt{p^2 + 1} - 1 - \kappa|x|^{-1} \right)_- - \left(\frac{1}{2}p^2 - \kappa|x|^{-1} \right)_- \right].$$

In (6) we used the notation $A_- := -A\chi_{(-\infty, 0)}(A)$ for the negative part of a self-adjoint operator A .

Several remarks apply:

- (1) As already mentioned in the introduction, the asymptotics of the ground-state energy $E^S(Z)$ of the Schrödinger atom up to $o(Z^2)$ is given by the Thomas-Fermi energy and the Scott correction. To state this result precisely we introduce the Thomas-Fermi functional (Lenz [31])

$$(7) \quad \mathcal{E}_{\text{TF}}(\rho) := \int_{\mathbb{R}^3} \left[\frac{3}{5} \gamma_{\text{TF}} \rho(x)^{5/3} - \frac{Z}{|x|} \rho(x) \right] dx + D(\rho, \rho)$$

where, in our units, $\gamma_{\text{TF}} = (6\pi^2/q)^{2/3}/2$ and where

$$D(\rho, \sigma) := \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\sigma(y)}{|x-y|} dx dy$$

is the Coulomb scalar product. We define

$$(8) \quad E_{\text{TF}}(Z) := \inf\{\mathcal{E}_{\text{TF}}(\rho) \mid \rho \in L^1(\mathbb{R}^3) \cap L^{5/3}(\mathbb{R}^3), \rho \geq 0\}$$

to be the minimal Thomas-Fermi energy. By scaling one finds that

$$E_{\text{TF}}(Z) = E_{\text{TF}}(1)Z^{7/3}.$$

The asymptotic formula

$$(9) \quad E^S(Z) = E_{\text{TF}}(Z) + \frac{1}{4}qZ^2 + O(Z^{47/24})$$

was proven in [48, 49]; for a lower bound only, see Hughes [26, 27]. Inserting this into (5) one finds that

$$(10) \quad E_{\kappa}^C(Z) = E_{\text{TF}}(Z) + \left(\frac{1}{4} - s(\kappa)\right) qZ^2 + o(Z^2).$$

- (2) The spectral shift $s(\kappa)$ is monotone increasing with respect to κ and strictly positive for $\kappa > 0$. Indeed, by scaling $x \mapsto x/\kappa$,

$$s(\kappa) = \text{tr} \left[\left(\sqrt{\kappa^{-2}p^2 + \kappa^{-4}} - \kappa^{-2} - |x|^{-1} \right)_- - \left(\frac{1}{2}p^2 - |x|^{-1} \right)_- \right],$$

and $\sqrt{\kappa^{-2}p^2 + \kappa^{-4}} - \kappa^{-2}$ is monotone decreasing with respect to κ .

- (3) It is part of our assertion that the operator in brackets in (6) belongs to the trace class. In the subcritical case $\kappa < 2/\pi$ this was already proved by Sørensen [43]. The finiteness of $s(2/\pi)$ should not be taken for granted: in fact, when substituting the Dirac operator for the Chandrasekar operator in (6) it was shown numerically that the corresponding spectral shift diverges at the critical coupling [43].

Since neither the Schrödinger nor the Chandrasekhar operator depend explicitly on spin, we shall assume henceforth $q = 1$; the general case follows along the same line. We prove Theorem 1.1 in Section 3 after having established a precise bound on the spectral shift for one-particle operators in the next section.

2. BOUND ON THE SPECTRAL SHIFT

For any real-valued potential v for which the following operators can be defined according to Friedrichs, we set

$$(11) \quad S(v) := \frac{1}{2}p^2 - v,$$

$$(12) \quad C(v) := \sqrt{p^2 + 1} - 1 - v,$$

the Schrödinger respectively Chandrasekar operator in $L^2(\mathbb{R}^3)$. We assume $c = 1$ throughout this section.

If the potential v is radially symmetric, both the Schrödinger and the Chandrasekhar operator commute with the angular momentum operators allowing for a decomposition into the corresponding invariant subspaces. For each $l \in \mathbb{N}_0$ the subspace \mathfrak{H}_l spanned by the spherical harmonics $Y_{l,m}$ with $m = -l, \dots, l$, is an invariant subspace of $S(v)$ and $C(v)$, and $\oplus_{l=0}^{\infty} \mathfrak{H}_l = L^2(\mathbb{R}^3)$. We write Λ_l for the orthogonal projection onto \mathfrak{H}_l and

$$(13) \quad \text{tr}_l(A) := \text{tr}(\Lambda_l A)$$

for the corresponding reduced trace.

Our main result in this section concerns the decay of the spectral shift

$$\text{tr}_l([C(v)]_- - [S(v)]_-)$$

as the angular momentum l increases. We shall prove

Theorem 2.1. *There exists a constant M such that for all $\mu \geq 0$ and for all $l \in \mathbb{N}_0$ and for all $v : [0, \infty) \rightarrow [0, \infty)$ satisfying*

$$(14) \quad v(r) \leq \frac{2}{\pi} r^{-1}$$

the sum of eigenvalue differences for angular momentum l is bounded according to

$$(15) \quad 0 \leq \text{tr}_l ([C(v) + \mu]_- - [S(v) + \mu]_-) \leq M(l+1)^{-2}.$$

This theorem shows that there is an effective cancelation in the difference in (15). Indeed, if $v(r) = \kappa r^{-1}$, then

$$\text{tr}_l [S(\kappa r^{-1})]_- = (2l+1) \frac{\kappa^2}{2} \sum_{n=1}^{\infty} \frac{1}{(n+l)^2}$$

and this does not decay at all as $l \rightarrow \infty$. We note also that (15) implies that the operator $\left(\sqrt{p^2 + 1} - 1 - \kappa|x|^{-1}\right)_- - \left(\frac{1}{2}p^2 - \kappa|x|^{-1}\right)_-$ appearing in Theorem 1.1 is trace class for any $\kappa \in (0, \frac{2}{\pi}]$.

2.1. Reminder on Lieb-Thirring Estimates. In the proof of Theorem 2.1 we use the following relativistic Lieb-Thirring inequalities due to Daubechies [7].

Proposition 2.2. *For any $\gamma > \frac{1}{2}$ there exists a constant L_γ such that for all $l \geq 0$*

$$(16) \quad \text{tr}_l [C(v)]_-^\gamma \leq L_\gamma (2l+1) \int_0^\infty \left[[v(r)]_+^{1+\gamma} + [v(r)]_+^{\frac{1}{2}+\gamma} \right] dr.$$

Proposition 2.2 is also valid for $\gamma = \frac{1}{2}$, but we will not need this fact.

Proof. Since $\text{tr}_l [C(v)]_-^\gamma \leq (2l+1) \text{tr}_0 [C(v)]_-^\gamma$, it suffices to verify the claim for $l = 0$. If we extend v to an even function \tilde{v} on \mathbb{R} , then $C(v)$ is unitarily equivalent to the part of the *whole-line* operator $\sqrt{p^2 + 1} - 1 - \tilde{v}$ on antisymmetric functions. In the whole-line case, the result follows by evaluating the integral in [7, Eq. (2.14)]. \square

Our treatment of the critical case $\kappa = \frac{2}{\pi}$ is based on the following inequality [37, Theorem 11] of Lieb and Yau.

Proposition 2.3. *Let I be a function with support in $\{x \in \mathbb{R}^3 : |x| \leq 1\}$. Then for all $\mu > 0$*

$$\text{tr} [I (|p| - \frac{2}{\pi}|x|^{-1} - \mu) \bar{I}]_- \leq \text{const } \mu^4 \int |I(x)|^2 dx.$$

2.2. Finiteness of Partial Traces. In (15) appears the trace of the difference of the operators $[C(v) + \mu]_-$ and $[S(v) + \mu]_-$. We begin by proving that both operators separately have finite traces. Since $S(v) \leq C(v)$ (see also (25) below) it suffices to prove this in the relativistic case.

Lemma 2.4. *For all $l \in \mathbb{N}_0$ one has $\text{tr}_l [C(\frac{2}{\pi}|x|^{-1})]_- < \infty$.*

Proof. Pick a Lipschitz function $\varphi : \mathbb{R}_+ \rightarrow [0, \pi/2]$ with Lipschitz constant ϕ_0 which vanishes for $r \leq 1/2$ and which is $\pi/2$ for $r \geq 1$. Then $I := \cos(\varphi)$ has compact support around the origin and, furthermore, it constitutes together with $A := \sin(\varphi)$ a quadratic partition of unity, i.e., $I^2 + A^2 = 1$. According to Lieb and Yau [37, Theorem 9] we have the localization formula

$$(17) \quad \langle \psi, (p^2 + 1)^{1/2} \psi \rangle = \langle I\psi, (p^2 + 1)^{1/2} I\psi \rangle + \langle A\psi, (p^2 + 1)^{1/2} A\psi \rangle - \langle \psi, L\psi \rangle$$

for $\psi \in L^2(\mathbb{R}^3)$. Here L is the bounded integral operator on $L^2(\mathbb{R}^3)$ with non-negative kernel given in terms of a Bessel function

$$(18) \quad L(x, y) := K_2(|x - y|) \frac{\sin^2[(\varphi(|x|) - \varphi(|y|))/2]}{\pi^2 |x - y|^2}.$$

We shall estimate this localization error by a multiplication operator. More precisely, we shall show that there exists a constant $M > 0$ such that

$$(19) \quad \langle \psi, L\psi \rangle \leq M \langle \psi, e^{-|x|} \psi \rangle.$$

To prove this, we note that by the Schwarz inequality we have

$$(20) \quad \begin{aligned} \langle \psi, L\psi \rangle &\leq \int_{\mathbb{R}^3} dx |\psi(x)|^2 \int_{\mathbb{R}^3} dy K_2(|x - y|) \frac{\sin^2((\varphi(|x|) - \varphi(|y|))/2)}{\pi^2 |x - y|^2} \\ &\leq \left(\frac{\phi_0}{2\pi}\right)^2 \int_{|x| < 1} dx |\psi(x)|^2 \int_{\mathbb{R}^3} dy K_2(|x - y|) \\ &\quad + \left(\frac{\phi_0}{2\pi}\right)^2 \int_{|x| \geq 1} dx |\psi(x)|^2 \int_{|y| < 1} dy K_2(|x - y|) \\ &=: \langle \psi, v_I \psi \rangle + \langle \psi, v_A \psi \rangle. \end{aligned}$$

Since $\int_0^\infty dr r^2 K_2(r) = 3\pi/2$ [38, Formula 11.4.22] we have

$$v_I(x) := \left(\frac{\phi_0}{2\pi}\right)^2 \chi_{\{|x| < 1\}}(x) \int_{\mathbb{R}^3} dy K_2(|x - y|) = \frac{3\phi_0^2}{2} \chi_{\{|x| < 1\}}(x).$$

Moreover, since $K_2(r) = 2/r^2 + O(1)$ as $r \downarrow 0$ and $K_2(r) \sim \sqrt{\pi/(2r)} \exp(-r)$ as $r \rightarrow \infty$ [42], the function

$$v_A(x) := \left(\frac{\phi_0}{2\pi}\right)^2 \chi_{\{|x| \geq 1\}}(x) \int_{|x+y| < 1} dy K_2(|y|)$$

is well-defined and satisfies $v_A(x) \leq \text{const } e^{-|x|}$. This proves (19).

Combining (17) and (19) we find that

$$(21) \quad \begin{aligned} &\text{tr}_l \left[C \left(\frac{2}{\pi} |x|^{-1} \right) \right]_- \\ &\leq \text{tr}_l \left[I \left(C \left(\frac{2}{\pi} |x|^{-1} + M e^{-|x|} \right) \right) I \right]_- + \text{tr}_l \left[A \left(C \left(\frac{2}{\pi} |x|^{-1} + M e^{-|x|} \right) \right) A \right]_- . \end{aligned}$$

To estimate the inner part we use that

$$I \left(C \left(\frac{2}{\pi} |x|^{-1} + M e^{-|x|} \right) \right) I \geq I \left(|p| - \frac{2}{\pi} |x|^{-1} - 1 - M e^{-1} \right) I.$$

It follows therefore from Proposition 2.3 that the corresponding trace is finite (even when summed over all l). For the outer part we use

$$A \left(C \left(\frac{2}{\pi} |x|^{-1} + M e^{-|x|} \right) \right) A \geq C \left(\chi_{\{|x| \geq \frac{1}{2}\}} \frac{2}{\pi} |x|^{-1} + M e^{-|x|} \right).$$

The corresponding trace is finite by Proposition 2.2. \square

2.3. Angular Momentum Barrier Inequalities. A straightforward consequence of Hardy's inequality, which we will frequently exploit, is

Lemma 2.5. *Let $l \in \mathbb{N}_0$. Then, as operators in \mathfrak{H}_l*

$$(22) \quad p^2 \geq (l + \tfrac{1}{2})^2 r^{-2}.$$

Proof. Writing the Laplacian in spherical coordinates we find that p^2 in \mathfrak{H}_l is unitarily equivalent to $p_r^2 + l(l+1)r^{-2}$ in $L^2(\mathbb{R}_+)$. The claim follows hence from Hardy's inequality, $p_r^2 \geq (2r)^{-2}$. \square

By operator monotonicity of the square root, (22) implies the (non-sharp) inequality $|p| \geq (l + \frac{1}{2})r^{-1}$ in \mathfrak{H}_l . We shall need an analogue of this inequality for the operator $C(0)$ instead of $|p|$. Note that $\sqrt{p^2 + 1} - 1$ behaves as $\frac{1}{2}p^2$ for small p . Since 'small p ' corresponds intuitively to 'large r ', we cannot expect that $C(0)$ controls an r^{-1} decay. But it *does* control an r^{-1} singularity. This is the content of

Lemma 2.6. *Let $l \in \mathbb{N}_0$, $R > 0$ and $M_l(R) := (l + \frac{1}{2})^2 / (R + \sqrt{R^2 + (l + \frac{1}{2})^2})$. Then, as operators in \mathfrak{H}_l*

$$(23) \quad C(0) \geq M_l(R) \chi_{\{r \leq R\}}(r) r^{-1}.$$

Proof. The inequality (22) and operator monotonicity of the square root imply in \mathfrak{H}_l

$$\sqrt{p^2 + 1} - 1 \geq \sqrt{(l + \tfrac{1}{2})^2 r^{-2} + 1} - 1;$$

the claim follows by determining the solution of the equation

$$\sqrt{(l + \tfrac{1}{2})^2 r^{-2} + 1} = 1 + M r^{-1}.$$

\square

The core of Theorem 2.1 is contained in the following

Lemma 2.7. *There exists a constant such that for all $v : [0, \infty) \rightarrow [0, \infty)$ satisfying (14) for all $\mu \geq 0$ and for all $l \in \mathbb{N}$ one has*

$$(24) \quad \begin{aligned} 0 &\leq \text{tr}_l ([C(v) + \mu]_- - [S(v) + \mu]_-) \\ &\leq \text{const} \left(\text{tr}_l [C(w_l)]_-^2 + (l + \tfrac{1}{2})^{-2} \text{tr}_l [C(w_l)]_- \right) \end{aligned}$$

where $w_l(r) := 10 r^{-1} \chi_{\{r \geq l^2/4\}}(r)$.

Proof. The identity

$$(25) \quad \tfrac{1}{2}p^2 = C(0) + \tfrac{1}{2}C(0)^2$$

implies the non-negativity asserted in (24).

To prove the second inequality in (24) we shall first assume (in addition to (14)) that v is a bounded function and that $\mu > 0$. Once the inequality is proved in this case (with a constant independent of μ and the supremum of v), we can apply it to the cut-off potential $v_M := \min\{v, M\}$.

By monotone convergence $C(v_M)$ and $S(v_M)$ converge to $C(v)$ and $S(v)$ in strong resolvent sense [8, Thm. 1.2.3], and therefore [45, Thm. VIII.20], [53, Thm. 2.7] for any $\mu > 0$, $\liminf_{M \rightarrow \infty} \text{tr}_l [C(v_M) + \mu]_- \geq \text{tr}_l [C(v) + \mu]_-$ and similarly for $S(v_M)$. But the reverse inequalities are also true, since $C(v_M) \geq C(v)$ and $S(v_M) \geq$

$S(v)$. Hence we conclude that $\text{tr}_l ([C(v_M) + \mu]_- - [S(v_M) + \mu]_-)$ converges to the corresponding quantity with v_M replaced by v . Finally, we can use Lemma 2.4 to extend the result to $\mu \rightarrow 0$.

Thus we may assume v to be bounded, $\mu > 0$ and denote by γ_l the orthogonal projection onto the eigenspace of $C(v)$ corresponding to angular momentum l and eigenvalues less or equal than $-\mu$. Since v is bounded, any eigenfunction of $C(v)$ lies in the form domain of $S(v)$. Hence the variational principle together with (25) yields

$$(26) \quad 2 \text{tr}_l ([C(v) + \mu]_- - [S(v) + \mu]_-) \leq \text{tr}_l [C(0)^2 \gamma_l].$$

Again the boundedness of v and the finite rank of γ_l imply that $\text{tr}_l [C(0)^2 \gamma_l]$ is finite. Using the eigenvalue equation and the bound (14) on the potential we estimate this term further as follows.

$$(27) \quad \text{tr}_l [C(0)^2 \gamma_l] \leq \text{tr}_l [C(v)]_-^2 + \text{tr}_l [v^2 \gamma_l] \leq \text{tr}_l [C(\frac{2}{\pi}|x|^{-1})]_-^2 + (\frac{2}{\pi})^2 \text{tr}_l [|x|^{-2} \gamma_l].$$

The last term in the above inequality is bounded using (22) and (25),

$$(28) \quad \| |x|^{-1} \psi_l \|^2 \leq (l + \frac{1}{2})^{-2} \| |p| \psi_l \|^2 = (l + \frac{1}{2})^{-2} (\|C(0) \psi_l\|^2 + 2 \langle \psi_l, C(0) \psi_l \rangle)$$

valid for $\psi_l \in \mathfrak{H}_l$. Since $l \geq 1$ we have $(\frac{2}{\pi})^2 (l + \frac{1}{2})^{-2} \leq \frac{1}{2}$ and thus the last two estimates may be summarized as

$$(29) \quad \text{tr}_l [C(0)^2 \gamma_l] \leq 2 \text{tr}_l [C(\frac{2}{\pi}|x|^{-1})]_-^2 + 4(\frac{2}{\pi})^2 (l + \frac{1}{2})^{-2} \text{tr}_l [C(0) \gamma_l].$$

In view of (26) the assertion will follow, if we can prove

$$(30) \quad \text{tr}_l [C(\frac{2}{\pi}|x|^{-1})]_-^2 \leq \text{tr}_l [C(w_l)]_-^2, \quad \text{tr}_l [C(0) \gamma_l] \leq \text{tr}_l [C(w_l)]_-.$$

We begin with the (more difficult) second inequality. We have

$$(31) \quad \text{tr}_l [C(0) \gamma_l] \leq \text{tr}_l [v \gamma_l] \leq \frac{2}{\pi} \text{tr}_l [|x|^{-1} \gamma_l] \leq \text{tr}_l [|x|^{-1} \gamma_l].$$

We apply Lemma 2.6 with $R = l^2/4$ to bound the last term. Since $M_l(l^2/4) \geq 5/4$ for $l \geq 1$ we obtain

$$(32) \quad \langle \psi_l, |x|^{-1} \psi_l \rangle \leq \frac{4}{5} \langle \psi_l, C(0) \psi_l \rangle + \langle \psi_l, \chi_{\{r \geq l^2/4\}}(|x|) |x|^{-1} \psi_l \rangle.$$

The last two estimates can be summarized as

$$(33) \quad \text{tr}_l [C(0) \gamma_l] \leq -\text{tr}_l [C(w_l) \gamma_l] \leq \text{tr}_l [C(w_l)]_- ,$$

which proves the second inequality in (30). We proceed similarly to prove the first one. Indeed, by (32)

$$(34) \quad C(\frac{2}{\pi}|x|^{-1}) \geq \frac{1}{5} C(0) + \chi_{\{r \leq l^2/4\}}(|x|) |x|^{-1} - \frac{2}{\pi} |x|^{-1} \geq \frac{1}{5} C(w_l)$$

and hence $\text{tr}_l [C(\frac{2}{\pi}|x|^{-1})]_-^2 \leq \frac{1}{25} \text{tr}_l [C(w_l)]_-^2$. This completes the proof of the lemma. \square

Now everything is in place for the

Proof of Theorem 2.1. The boundedness of the trace in (15) for $l = 0$ is implied by Lemma 2.4 below, and its non-negativity follows from (25). For $l \geq 1$ we use Lemma 2.7 and note that

$$(35) \quad \text{tr}_l [C(w_l)]_-^2 \leq \text{const } l^{-2}, \quad \text{tr}_l [C(w_l)]_- \leq \text{const}$$

by Proposition 2.2. \square

3. PROOF OF THE MAIN RESULTS: RENORMALIZATION OF THE RELATIVISTIC OPERATOR

The strategy for our proof of the main results is to use the Schrödinger operator as a regularization for the relativistic problem, i.e., we will use it to eliminate the main contribution to the energy – the Thomas-Fermi energy – and to focus only on the energy shift of the low lying states where the electron-electron interaction plays no role and the unscreened problem remains.

Recall that Theorem 1.1 for $q = 1$ reads

$$(36) \quad \lim_{Z \rightarrow \infty} \frac{E^S(Z) - E_\kappa^C(Z)}{Z^2} = s(\kappa).$$

We will show this claim in two steps, namely that the upper limit and the lower limits exist and are given by the same expression, namely the coefficient of the Z^2 -correction claimed in the theorem. That this coefficient is finite was already remarked after Theorem 2.1.

3.1. Upper Bound on the Energy Difference – Lower Bound on the Relativistic Energy. Lieb and Simon [36] showed that the Thomas-Fermi minimization problem (8) has a unique minimizer ρ_Z , the Thomas-Fermi density. It fulfills the scaling relation

$$(37) \quad \rho_Z(x) := Z^2 \rho_1(Z^{1/3}x).$$

We define the radius of the Thomas-Fermi exchange hole at point $x \in \mathbb{R}^3$ as the unique minimal radius $R_Z(x)$ for which

$$(38) \quad \int_{|x-y| \leq R_Z(x)} \rho_Z(y) dy = \frac{1}{2}.$$

We denote the exchange-hole-reduced Thomas-Fermi screening potential by

$$(39) \quad \chi_{\text{TF}}(x) := \int_{|x-y| > R_Z(x)} \frac{\rho_Z(y)}{|x-y|} dy$$

and the corresponding one-particle operators by

$$(40) \quad S_{\text{TF}} = S(Z|x|^{-1} - \chi_{\text{TF}})$$

$$(41) \quad C_{\text{TF}} = C_c(Z|x|^{-1} - \chi_{\text{TF}})$$

both self-adjointly realized in $L^2(\mathbb{R}^3)$. Here we use a notation similar to that in Section 2,

$$(42) \quad C_c(v) := \sqrt{p^2 c^2 + c^4} - c^2 - v.$$

We remark that we slightly deviate from the more usual choice $Z|x|^{-1} - \rho_Z * |\cdot|^{-1}(x)$ for the screened potential. This is motivated by the correlation inequality (44) below. The concept of an exchange hole can be traced back to Slater [54]. It also has been used to estimate the exchange-correlation energy (Lieb [32], Lieb and Oxford [35]).

We shall express the many-particle ground-state energy in terms of quantities involving the above one-particle operators. In the relativistic case we use the correlation inequality of [39] to obtain a lower bound on the many-particle ground-state energy.

Lemma 3.1. *For all $L \in \mathbb{N}$,*

$$(43) \quad E_\kappa^C(Z) \geq - \sum_{l=0}^{L-1} \operatorname{tr}_l [C_c(Z|x|^{-1})]_- - \sum_{l=L}^{\infty} \operatorname{tr}_l [C_{\text{TF}}]_- - D(\rho_Z, \rho_Z).$$

Proof. We use the correlation inequality [39, Equation (14)]

$$(44) \quad \sum_{1 \leq \mu < \nu \leq N} |x_\mu - x_\nu|^{-1} \geq \sum_{\nu=1}^N \chi_{\text{TF}}(x_\nu) - D(\rho_Z, \rho_Z),$$

to bound $E_\kappa^C(Z)$ from below by the ground-state energy of

$$\sum_{\nu=1}^N (C_{\text{TF}})_\nu - D(\rho_Z, \rho_Z).$$

This yields

$$(45) \quad E_\kappa^C(Z) \geq -\operatorname{tr}[C_{\text{TF}}]_- - D(\rho_Z, \rho_Z).$$

We split the trace according to angular momentum and use the operator inequality $C_{\text{TF}} \geq C_c(Z|x|^{-1})$ for all $l \leq L-1$ to obtain the assertion. \square

In the non-relativistic case, we recall

Proposition 3.2. *Let $L := \lceil Z^{1/9} \rceil$. Then, as $Z \rightarrow \infty$,*

$$(46) \quad E^S(Z) = - \sum_{l=0}^{L-1} \operatorname{tr}_l [S(Z|x|^{-1})]_- - \sum_{l=L}^{\infty} \operatorname{tr}_l [S_{\text{TF}}]_- - D(\rho_Z, \rho_Z) + O(Z^{47/24}).$$

Proof. The same argument as in Lemma 3.1 yields the lower bound

$$(47) \quad E^S(Z) \geq - \sum_{l=0}^{L-1} \operatorname{tr}_l [S(Z|x|^{-1})]_- - \sum_{l=L}^{\infty} \operatorname{tr}_l [S_{\text{TF}}]_- - D(\rho_Z, \rho_Z).$$

Note that the $\chi_{\text{TF}} \leq \rho_Z * |\cdot|^{-1}$. Hence [51, Theorem 1] and the proof of this theorem (in particular, [51, Lemma 2], see also [52]) show that one can further estimate

$$(48) \quad \begin{aligned} & - \sum_{l=0}^{L-1} \operatorname{tr}_l [S(Z|x|^{-1})]_- - \sum_{l=L}^{\infty} \operatorname{tr}_l [S_{\text{TF}}]_- - D(\rho_Z, \rho_Z) \\ & \geq E_{\text{TF}}(Z) + \frac{1}{4}Z^2 - \text{const } Z^{17/9} \log Z. \end{aligned}$$

On the other hand, one has the upper bound [48, Lemmas 3.1 and 4.1]

$$(49) \quad E^S(Z) \leq E_{\text{TF}}(Z) + \frac{1}{4}Z^2 + \text{const } Z^{47/24}$$

Combining this with (47) and (48) we obtain the assertion. \square

Proof of Theorem 1.1 – first part. Choosing $L = \lceil Z^{1/9} \rceil$ and combining Lemma 3.1 and Proposition 3.2 we obtain

$$(50) \quad \begin{aligned} E^S(Z) - E_\kappa^C(Z) & \leq - \sum_{l=0}^{L-1} \operatorname{tr}_l \left([S(Z|x|^{-1})]_- - [C_c(Z|x|^{-1})]_- \right) \\ & \quad - \sum_{l=L}^{\infty} \operatorname{tr}_l ([S_{\text{TF}}]_- - [C_{\text{TF}}]_-) + \text{const } Z^{47/24}. \end{aligned}$$

We note that by scaling $x \mapsto x/c$, the operators S_{TF} and C_{TF} are unitarily equivalent to the operators $\kappa^{-2}Z^2S(\kappa|x|^{-1} - \chi_Z)$ and $\kappa^{-2}Z^2C_1(\kappa|x|^{-1} - \chi_Z)$, both acting in $L^2(\mathbb{R}^3)$, where

$$(51) \quad \chi_Z(x) := \kappa^2 Z^{-2} \chi_{\text{TF}}(\kappa x/Z).$$

This implies

$$(52) \quad \limsup_{Z \rightarrow \infty} \frac{E^S(Z) - E_\kappa^C(Z)}{Z^2} \leq \kappa^{-2} \limsup_{Z \rightarrow \infty} (\Sigma_1(Z) + \Sigma_2(Z))$$

where

$$\begin{aligned} \Sigma_1(Z) &:= \sum_{l=0}^{L-1} \text{tr}_l \left([C_1(\kappa|x|^{-1})]_- - [S(\kappa|x|^{-1})]_- \right) \\ \Sigma_2(Z) &:= \sum_{l=L}^{\infty} \text{tr}_l \left([C_1(\kappa|x|^{-1} - \chi_Z)]_- - [S(\kappa|x|^{-1} - \chi_Z)]_- \right). \end{aligned}$$

Theorem 2.1 implies that the summands in both sums on the right-hand side are non-negative and bounded by $\text{const } (l+1)^{-2}$ independently of Z . Therefore the first sum actually converges

$$(53) \quad \limsup_{Z \rightarrow \infty} \Sigma_1(Z) = \sum_{l=0}^{\infty} \text{tr}_l \left([C_1(\kappa|x|^{-1})]_- - [S(\kappa|x|^{-1})]_- \right).$$

Moreover, the second sum converges to zero,

$$(54) \quad \limsup_{Z \rightarrow \infty} \Sigma_2(Z) \leq \text{const} \limsup_{Z \rightarrow \infty} \sum_{l=L}^{\infty} (l+1)^{-2} = 0.$$

This concludes the proof of the upper bound on the energy difference. \square

We remark that $\Sigma_2(Z) \leq \text{const } Z^{-1/9}$, hence we have actually shown that

$$(55) \quad E^S(Z) - E_\kappa^C(Z) \leq s(\kappa)Z^2 + \text{const } Z^{47/24}.$$

3.2. Lower Bound on the Energy Difference – Upper Bound on the Relativistic Energy. Following [48] we define two one-particle density matrices d^S and d^C as sums

$$(56) \quad d^\# = \sum_{l=0}^{\infty} d_l^\#.$$

As above, we use the convention that $\#$ refers either to the Schrödinger case or to the Chandrasekhar case. The operators $d_l^\#$ are defined in $L^2(\mathbb{R}^3)$ through their integral kernels

$$(57) \quad d_l^\#(x, y) := \sum_{n=1}^{\infty} w_{n,l} \sum_{m=-l}^l \psi_{n,l,m}^\#(x) \overline{\psi_{n,l,m}^\#(y)}.$$

The weights $w_{n,l}$ and the functions $\psi_{n,l,m}^\#$ are defined separately for angular momentum $l < L$ and $l \geq L$ where L will be chosen later in a Z -dependent way.

Case $l < L$: We define $\psi_{n,l,m}^\#$ as the n -th eigenfunction of $S(Z|x|^{-1})$ restricted to angular momentum (l, m) , respectively of $C_c(Z|x|^{-1})$ restricted to angular momentum (l, m) , with the normalization $\|\psi_{n,l,m}^\#\|_2 = 1$. Note that this function is of the form $\psi_{n,l,m}^\#(x) = \varphi_{n,l}(|x|)Y_{l,m}(x/|x|)$ with a radial function $\varphi_{n,l}$. The weights $w_{n,l}$ are defined independently of m by

$$(58) \quad w_{n,l} := \begin{cases} 1 & n \leq K - l, \\ 0 & n > K - l. \end{cases}$$

where $K := [dZ^{1/3}]$ with d some positive constant independent of Z .

Case $l \geq L$: We choose $\psi_{n,l,m}^\#(x) = \varphi_{n,l}(|x|)Y_{l,m}(x/|x|)$ where the functions $\varphi_{n,l}$, as well as the weights $w_{n,l}$, are defined exactly as in [48, Section 2] independently of $\#$. (The exact form of the functions and the values of the weights for $l \geq L$ are irrelevant in our context.)

Note that the above construction guarantes $d^\#$ to be density matrices, i.e., $0 \leq d^\# \leq 1$. Moreover, by the choice of L , K , and $w_{n,l}$ one can assure that $\text{tr } d^\# \leq Z$. (For $\# = S$ this is proved in [48, Corollary 4.1], and follows hence also for $\# = C$.)

Since $d_l^\#$ is independent of $\#$ for $l \geq L$ we drop the superscript in this case. Moreover, we shall use the notations

$$d_{<}^\# := \sum_{l=0}^{L-1} d_l^\#, \quad d_{>} := \sum_{l=L}^{\infty} d_l,$$

and

$$\rho_l^\#(x) := d_l^\#(x, x), \quad \rho_{<}^\#(x) := d_{<}^\#(x, x), \quad \rho_{>}(x) := d_{>}(x, x).$$

We recall now that the density matrix d^S gives an energy which is correct up to the order we are interested in. More precisely, one has

Proposition 3.3. *Let $L := [Z^{1/12}]$. Then, for sufficiently large Z ,*

$$(59) \quad E^S(Z) = \text{tr}[S(Z|x|^{-1})d^S] + D(\rho^S, \rho^S) + O(Z^{47/24}).$$

Proof. It is shown in [48] that for sufficiently large Z ,

$$E^S(Z) \leq \text{tr}[S(Z|x|^{-1})d^S] + D(\rho^S, \rho^S) \leq E_{\text{TF}}(Z) + \frac{1}{4}Z^2 + \text{const } Z^{47/24}.$$

Combining this with the lower bound on $E^S(Z)$ which was recalled in (47) and (48), we obtain the assertion. \square

We decrease the ground state energy further by dropping a part of the Coulomb energy,

$$(60) \quad E^S(Z) \geq \text{tr}[S(Z|x|^{-1})d_{<}^S] + \text{tr}[S(Z|x|^{-1})d_{>}] + D(\rho_{>}, \rho_{>}) - \text{const } Z^{47/24}.$$

For an upper bound in the relativistic case we employ a variational principle to obtain

Lemma 3.4. *For sufficiently large Z*

$$E_\kappa^C(Z) \leq \text{tr}[C_c(Z/|x|)d_{<}^C] + \text{tr}[S(Z/|x|)d_{>}] + D(\rho_{>}, \rho_{>}) + 2D(\rho_{<}^C, \rho_{>}) + D(\rho_{<}^C, \rho_{<}^C).$$

Proof. As noted above, d^C satisfies $0 \leq d^C \leq 1$ and $\text{tr } d^C \leq Z$ for sufficiently large Z [48, Corollary 4.1]. Using that the Hartree-Fock functional bounds the ground state energy from above – even if non-idempotent density matrices are inserted, a

fact that was proven by Lieb [33] (see also Bach [3]) – and estimating the indirect part of the Coulomb energy by zero we obtain

$$(61) \quad E_\kappa^C(Z) \leq \text{tr}[C_c(Z|x|^{-1})d^C] + D(\rho^C, \rho^C).$$

Both terms on the right-hand side are split according to $d^C = d_{<}^C + d_{>}^C$. To obtain the desired upper bound we use the inequality $\frac{1}{2}p^2 \geq \sqrt{c^2p^2 + c^4} - c^2$ for large angular momenta. \square

The following lemma shows the irrelevance of the interaction energy of the low lying states with all other electrons (including themselves). The proof follows the strategy pursued in [48], namely to estimate it by the lowest Coulomb energy of a particle in the field of an external point charge Z , and then simply multiplying by the particle number. There is, however, one important change in the channel $l = 0$. Because of the singular nature of the lowest eigenfunctions, their expectations in potentials with Coulomb singularities does not exist. To circumvent this problem we use the Hardy-Littlewood-Sobolev inequality followed by a recent Sobolev-type inequality [24].

Lemma 3.5. *One has $D(\rho_{<}^C, \rho^C) \leq \text{const } Z^{11/6} \log Z$.*

Proof. We treat the terms $D(\rho_{<}^C, \rho_{<}^C)$ and $D(\rho_{<}^C, \rho_{>}^C)$ separately. For the latter one we recall that

$$(62) \quad \int \rho_l^C(x) dx = (2l+1)(K-l), \quad 0 \leq l < L,$$

where $K = O(Z^{1/3})$ and that by Proposition 3.4 in [48]

$$(63) \quad \sum_{l=L}^{\infty} \int \frac{\rho_l(x)}{|x|} dx \leq \int \frac{\rho^S(x)}{|x|} dx \leq \text{const } Z^{4/3}.$$

The densities $\rho_l^\#$ are spherically symmetric because of the addition formula for the spherical harmonics. Hence, using Newton's theorem [41], we have

$$(64) \quad \begin{aligned} D(\rho_{<}^C, \rho_{>}^C) &\leq \frac{1}{2} \int \rho_{<}^C(x) dx \int \frac{\rho_{>}^C(y)}{|y|} dy \\ &\leq \text{const} \sum_{l=0}^{L-1} (2l+1)(K-l) Z^{4/3} \leq O(L^2 K Z^{4/3}) = O(Z^{11/6}). \end{aligned}$$

We set $\rho_{<>}^C := \rho_{<}^C - \rho_0^C$ and estimate

$$(65) \quad D(\rho_{<}^C, \rho_{<}^C) \leq 2D(\rho_0^C, \rho_0^C) + 2D(\rho_{<>}^C, \rho_{<>}^C).$$

This allows to treat the contributions from $l = 0$ and $1 \leq l < L$ separately. Using a scaled version of Lemma 2.6 with $R_l := ((l + \frac{1}{2})^2 - 4\kappa^2) / 4\kappa$ we obtain for $1 \leq l < L$

$$\begin{aligned} \text{tr}(|x|^{-1} d_l^C) &\leq \frac{1}{2Z} \text{tr}[C_c(0) d_l^C] + \text{tr}(\chi_{\{|x| > R_l/c\}} |x|^{-1} d_l^C) \\ &\leq \frac{1}{2} \text{tr}(|x|^{-1} d_l^C) + \frac{c}{R_l} \text{tr} d_l^C, \end{aligned}$$

where the last inequality used the fact that eigenfunctions of d_l^C are also eigenfunctions of $C_c(Z|x|^{-1})$ with negative eigenvalue. Hence, summing over l and noting

that $R_l^{-1} \leq \text{const } l^{-2}$,

$$\int \frac{\rho_{<>}(y)}{|y|} dy = \sum_{l=1}^L \text{tr}(|x|^{-1} d_l^C) \leq \text{const } Z \sum_{l=1}^{L-1} l^{-2} \int \rho_l^C(x) dx.$$

Thus by (62) and again by Newton's theorem

$$\begin{aligned} D(\rho_{<>}^C, \rho_{<>}^C) &\leq \frac{1}{2} \int \rho_{<>}^C(x) dx \int \frac{\rho_{<>}(y)}{|y|} dy \\ &\leq \text{const } K L^2 K Z \log L \leq \text{const } Z^{11/6} \log Z. \end{aligned}$$

Finally, we treat the term corresponding to $l = 0$. By the Hardy-Littlewood-Sobolev inequality (c.f. [34]) and by Hölder's inequality

$$\begin{aligned} D(\rho_0^C, \rho_0^C) &\leq \text{const } \|\rho_0^C\|_{6/5}^2 = \text{const } \left(\int \left(\sum_{n=1}^K |\psi_{n,0,0}^C(x)|^2 \right)^{6/5} dx \right)^{5/3} \\ &\leq \text{const } K^{1/3} \left(\sum_{n=1}^K \int |\psi_{n,0,0}^C(x)|^{12/5} dx \right)^{5/3}. \end{aligned}$$

Now we use the Sobolev-type inequality [24, Eq. (2.8)]

$$(66) \quad \|u\|_{12/5}^2 \leq \text{const } \langle u, (|p| - \frac{2}{\pi}|x|^{-1})u \rangle^{1/2} \|u\|$$

where the first factor on the right-hand side is to be understood in form sense. Using that $|p| - \frac{2}{\pi}|x|^{-1} \leq c^{-1}C_c(Z|x|^{-1}) + c$ and that $\psi_{n,0,0}^C$ is a normalized eigenfunction of $C_c(Z|x|^{-1})$ we deduce

$$(67) \quad \|\psi_{n,0,0}^C\|_{12/5} \leq \text{const } c^{1/4}.$$

Combining the previous relations we arrive at

$$(68) \quad D(\rho_0^C, \rho_0^C) \leq \text{const } K^{1/3} (K c^{3/5})^{5/3} \leq \text{const } Z^{5/3}.$$

This completes the proof of the lemma. \square

Proof of Theorem 1.1 – second part. It follows from Lemma 3.5 that

$$2D(\rho_{<}^C, \rho_{>}^C) + D(\rho_{<}^C, \rho_{<}^C) = O(Z^{11/6} \log Z).$$

Hence Lemma 3.4 together with (60) implies

$$\begin{aligned} &\liminf_{Z \rightarrow \infty} Z^{-2} [E^S(Z) - E_\kappa^C(Z)] \\ &\geq \liminf_{Z \rightarrow \infty} Z^{-2} \left\{ \text{tr} [S(Z|x|^{-1}) d_{<}^S] - \text{tr} [C_c(Z|x|^{-1}) d_{<}^C] \right\} \\ &= \liminf_{Z \rightarrow \infty} \sum_{l=0}^{L-1} (2l+1) \sum_{n=1}^{K-l} Z^{-2} [\langle \psi_{n,l,m}^S, S(Z|x|^{-1}) \psi_{n,l,m}^S \rangle \\ &\quad - \langle \psi_{n,l,m}^C, C_c(Z|x|^{-1}) \psi_{n,l,m}^C \rangle]. \end{aligned}$$

The claim now follows from the scaling $x \mapsto x/c$ and Fatou's lemma. \square

In order to get an explicit remainder estimate one could bound the sum

$$(69) \quad \sum_{l=0}^{L-1} (2l+1) \sum_{n=K-l+1}^{\infty} [\langle \psi_{n,l,m}^S, S(Z|x|^{-1}) \psi_{n,l,m}^S \rangle - \langle \psi_{n,l,m}^C, C_c(Z|x|^{-1}) \psi_{n,l,m}^C \rangle]$$

from above. This is certainly not difficult but for brevity we refrain from doing so. The sum corresponding to $l \geq L$ can be bounded using Theorem 2.1.

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